

# PATENT SPECIFICATION

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(19)



## (54) DETERGENT COMPOSITION

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E/C 4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to detergent compositions comprising vinyl polymers as anti-redeposition agents.

Modern textiles, particularly those composed of synthetic fabrics or a mixture of natural and synthetic fabrics, or chemically modified cotton, show a tendency to greying on washing.

Hitherto sodium carboxymethylcellulose has been used extensively in detergent compositions to reduce redeposition of soil during the washing process. However, whereas it is a very effective anti-redeposition agent for cotton and similar fabrics, it is ineffective as an anti-redeposition agent for synthetic, especially polyester fabrics. In recent years vinyl compounds, viz polyvinyl alcohol and polyvinyl-pyrrolidone have been proposed as soil-suspending agents for the prevention of soil redeposition, the success of which has been very slight. Moreover, it has now been established that, particularly the higher molecular weight polyvinyl alcohols show drawbacks during the processing and use of detergent compositions containing these materials. These substances tend to agglomerate in the slurry, which may be caused by their susceptibility of being salted out by electrolytes. The result is that coarse particles are formed which in some instances grow into large lumps attaching to the stirring elements of the slurry mixer. When added as a fine powder to the final composition to overcome this difficulty, their tendency to agglomerate still causes the formation of undissolved flakes during the washing process, which tend to attach to the laundry article, particularly to knitted fine wash garments.

It has now been found that copolymers of vinylpyrrolidone and vinylacetate are good anti-redeposition agents for synthetic and simi-

lar fabrics without showing the above drawbacks. These copolymers used in small amounts already prevent redeposition of soil on synthetic fabrics as sodium carboxymethylcellulose does on cotton. The specific or exact degree of polymerisation is not critical provided the material has the desired water solubility, ie it is water-soluble at the relatively low concentrations which occur in practice for detergent compositions. Generally the suitable vinylpyrrolidone/vinylacetate copolymers have an average molecular weight usually within the range of about 10,000 to about 400,000 and preferably from about 20,000 to 200,000. Such copolymers are known commercially but their use as anti-redeposition agents has not hitherto been disclosed. Their degree of effectiveness in reducing redeposition of soil depends on the ratio of vinylpyrrolidone (VP) and vinylacetate (VA) portion in the copolymer. Optimum of activity was noted at a VP:VA mol. ratio of 50:50. The preferred copolymers of the invention are those having VP:VA mol. ratios of between 10:90 and 90:10, more preferably between 30:70 and 70:30.

The VP/VA copolymers can be incorporated in liquid as well as particulate or solid detergent compositions. Used in particulate detergent compositions they may be admixed with the other ingredients in the conventional manner during the slurry-making preparation, followed by spray-drying. Some degree of hydrolysis of the acetate-portion of the copolymer may have occurred during the processing, without affecting the physical properties of the slurry or of the powder characteristics and its performance. The spray-dried powder shows no increase in hygroscopicity at all by the VP/VA copolymer content and maintains its free-flowing properties on storage.

The invention therefore provides a detergent composition comprising essentially a detergent active compound and a copolymer of vinylpyrrolidone and vinylacetate as hereinbefore defined.

Generally the amount of the vinyl-

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pyrrolidone/vinylacetate copolymer used as anti-redeposition agent in the composition should be a minor proportion of the composition, e.g. 0.1 to 5.0% by weight of the detergent composition, preferably from 0.2% up to 2.0%.

The detergent active compound in the composition according to the invention can be any of the conventional anionic, nonionic, cationic or ampholytic detergent active compounds normally included in fabric washing detergent compositions. Examples of suitable detergent active compounds are: alkylaryl sulphonates; alkyl or alkane sulphonates; alkyl sulphates; alkyl phosphates; the mixtures of anionic detergent active compounds produced by the sulphonation with sulphur trioxide, and subsequent hydrolysis and neutralisation of unsaturated hydrocarbons (commonly called olefin sulphonates); ethoxylated alcohols; ethoxylated alkyl phenols; ethoxylated amines; ethoxylated fatty acid amides; sulphates and phosphates of these ethoxylated materials; amine oxides; isothionates;  $C_{8}-C_{30}$  fatty acid soaps; taurines; betaines and sulphobetaines. Mixtures of these detergent active compounds may be used, if desired. They normally comprise 2 to 60% by weight of the detergent composition, but soap powders or soap flakes generally have

a much higher active detergent content, i.e. up to 95%.

In addition to the detergent active compound and the VP/VA copolymer, a composition of the invention may comprise any of the other conventional detergent composition ingredients, such as fatty acid amide lather boosters, e.g. coconut ethanolamide and palm kernel ethanolamide; inorganic and organic detergency builders such as sodium tripolyphosphate, trisodium orthophosphate and sodium nitrilotriacetate; hydrotropes such as sodium xylene sulphonate, sodium toluene sulphonate etc.; additives for inhibiting corrosion and fabric damage such as silicates; inorganic salts such as sodium sulphate and sodium carbonate; bleaches such as sodium perborate, sodium percarbonate and sodium chlorocyanurates; and, usually present in minor amounts, perfumes, colourants, fluorescers, germicides, enzymes and other anti-redeposition agents, such as sodium or potassium carboxymethylcellulose. This latter agent may be present in the composition in amounts of the same order as the anti-redeposition agent of the invention, viz 0.1—5.0% by weight, without affecting each other's performance.

The following Examples illustrate aspects of the invention in greater detail.

#### EXAMPLES I—II

The anti-redeposition characteristics of two VP/VA copolymers were compared with those of polyvinylpyrrolidone in a conventional nonionic base powdered detergent formulation using the following test method. A bowl washing machine provided with a mechanical stirrer was used.

<i>Fabrics washed:</i>	Treated cotton (chemically modified cross-linked cotton) "Nylon" Polyester
<i>Wash load:</i>	Each fabric test piece is 30 × 30 cm
<i>Water hardness:</i>	16° German hardness
<i>Cloth : liquor ratio:</i>	about 1 : 50
<i>Dosage:</i>	5 grams washing powder per liter
<i>Soil:</i>	$1.8 \times 10^{-3}\%$ standard graphite soil
<i>Temperature:</i>	60°C
<i>Washing time:</i>	15 minutes
<i>Rinsing:</i>	2 × with 4 litres cold water
<i>Rating:</i>	Measuring the reduction in whiteness degree using the "Lange" photometer after 5 washes

Example	1	2	A	B	C
<b>Components (%)</b>					
Nonylphenol-10 ethylene oxide	10.0	10.0	10.0	10.0	10.0
Sodium carbonate	6.0	6.0	6.0	6.0	6.0
Sodium sulphate	24.0	24.0	24.0	24.0	24.0
Waterglass ( $\text{SiO}_2:\text{Na}_2\text{O}=2.3:1$ )	3.0	3.0	3.0	3.0	3.0
Sodium carboxymethylcellulose	1.8	1.8	1.8	1.8	1.8
Sodium tripolyphosphate	50.0	50.0	50.0	50.0	50.2
Proteolytic enzyme	2.2	2.2	2.2	2.2	2.2
Water, perfume, etc.	3.8	3.8	3.8	3.8	3.8
Anti-redeposition agent <sup>1)</sup>	0.2	0.2	0.2	0.2	—

<sup>1)</sup> *Example 1:* VP/VA copolymer 60:40 (obtained from *Badische Anilin und Soda Fabriken* and sold under the trade name *Luviskol VA 64*)

*Example 2:* VP/VA copolymer 50:50 (obtained from *General Aniline & Film Corp.* and sold under the trade name *Elfa E-535*)

*Example A:* Polyvinylpyrrolidone (obtained from *BASF* and sold under the trade name *Luviskol K 30*)

*Example B:* Polyvinylpyrrolidone (obtained from *Basf* and sold under the trade name *Luviskol K90*)

TABLE I

Reduction in whiteness degree of test cloths after 5 consecutive washes

Example	Treated Cotton	"Nylon"	Polyester
1	13	21	38
2	11	23	41
A	48	67	63
B	27	51	45
C	67	76	60

The above table clearly shows the good anti-redeposition effect of the copolymers according to the invention in a nonionic detergent composition.

## EXAMPLE III—VI

The anti-redeposition characteristics of four VP/VA copolymers were compared with those of other polymeric compounds in a conventional powdered detergent composition containing soap, using the test method as explained in Example I—II.

Example	3	4	5	6	D	E	F
<b>Components. (%)</b>							
Sodium C <sub>12</sub> -alkylbenzene sulphonate	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Nonylphenol-10 ethylene oxide	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Soap (C <sub>12</sub> —C <sub>18</sub> fatty acids)	11.5	11.5	11.5	11.5	11.5	11.5	11.5
Sodium tripolyphosphate	50.0	50.0	50.0	50.0	50.0	50.0	50.2
Sodium sulphate	6.9	6.9	6.9	6.9	6.9	6.9	6.9
Waterglass (SiO <sub>2</sub> :Na <sub>2</sub> O=2.3:1)	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Sodium carboxymethylcellulose	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Ethylenediamine tetraacetic acid	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water, perfume, etc.	12.9	12.9	12.9	12.9	12.9	12.9	12.9
Anti-redeposition agent <sup>1)</sup>	0.2	0.2	0.2	0.2	0.2	0.2	—

<sup>1)</sup> *Example 3:* VP/VA copolymer 50:50 — (ex GAF; sold under the trade name Elfa E 535)

*Example 4:* VP/VA copolymer 20:80 — (ex BASF; sold under the trade name Luviskol VA 28)

*Example 5:* VP/VA copolymer 50:50 — (ex BASF; sold under the trade name Luviskol VA 55E)

*Example 6:* VP/VA copolymer 60:40 — (ex BASF; sold under the trade name Luviskol VA 64)

*Example D:* Alkylmonoester of poly(methylvinylether) — (ex GAF, sold under code number ES 225)

*Example E:* Styrene-acrylic ester copolymer — (ex Hoechst, sold under code number DM 60)

TABLE II

Reduction in whiteness degree of test cloths after 5 consecutive washes

Example	Treated Cotton	Cotton/Nylon	Cotton/Polyester
3	5.7	5.6	5.0
4	25.0	20.0	10.0
5	9.0	5.5	2.2
6	8.4	6.7	3.3
D	30.1	32.2	18.0
E	27.9	29.8	15.6
F	30.1	31.4	20.0

The above Table II shows that even in soap containing compositions the effect of the VP/VA copolymers is still clearly noticeable.

## EXAMPLE VII

The anti-redeposition characteristics of composition of Example V was tested in washing naturally soiled fabrics in a Schulthess drum-type washing machine set for the synthetic wash cycle with a maximum temperature of 60°C. The whiteness degree after 25 and 50 washes, measured with the "Elrepho"-photometer were compared with a similar composition without a VP/VA copolymer being present, except for sodium carboxymethylcellulose which was present as an anti-redeposition agent for cotton fabrics in conventional compositions (composition F). These results are shown in Table III.

Test Conditions

Normally soiled white laundry goods were washed together with samples of cotton, nylon, polyester, and Splendesto fabrics.

Wash load: 4 kg

Detergent product concentration: 5 g/litre

Water hardness: 20° German Hardness

Bath ratio: 1 : 6

Washing temperature: 60°C.

TABLE III

Whitening degree measured with the "Elrepho"-photometer

	After 25 washes			After 50 washes		
	Composition 5 with VP/VA	Composition F without VP/VA	Diff.	Composition 5 with VP/VA	Composition F without VP/VA	Diff.
Cotton	178	174	4	171	166	5
Nylon	141	123	18	138	127	11
Polyester	155	150	5	161	150	11
Splendesto	174	175	-1	179	174	5

## EXAMPLES VIII—XI

The following powdered detergent compositions were made without difficulty and were equally good in powder structure and performance.

Example	8	9	10	11
Component (%)				
Sodium dodecylbenzene sulphonate	7	—	6	20
Tallow soap	—	10	—	—
Nonyl phenol-10 ethylene oxide	5	10	3	—
C <sub>16</sub> —C <sub>18</sub> alkylphosphate	2	—	—	—
Sodium tripolyphosphate	40	30	30	50
Nitrilotriacetate (NTA)	—	—	10	—
Sodium sulphate	—	12.5	30	7.3
Waterglass	4	6	9	10.0
Ethylene diamine tetraacetate	0.2	0.2	0.5	0.2
Sodium perborate	30.0	20	—	—
Water + perfume	9.5	9.8	10.0	10.0
VP/VA copolymer 50 : 50	0.3	0.5	0.5	1.0
Carboxymethylcellulose	2.0	1.0	1.0	1.5

## EXAMPLES XII—XIV

Liquid preparations incorporating VP/VA copolymers devised for fine laundering.

Example	12	13	14
Components (%)			
Dodecyl benzene sulphonate	7.0	10.0	10.0
Sodium lauryl ether sulphate <sup>1</sup>	3.0	5.0	—
Lauryl sulphate	4.0	—	—
Nonylphenol-11 ethylene oxide	5.0	5.0	4.0
Alkylether phosphate <sup>2</sup>	—	—	15.0
Urea	5.0	3.0	5.0
Sodium xylene sulphonate	3.0	5.0	—
Ethyl alcohol	6.0	5.0	—
Ethylene diamine tetraacetate	0.2	—	0.2
Thickening agent	0.8	—	—
Sodium nitrilotriacetate	—	10.0	—
Sodium tripolyphosphate	—	—	15.0
Anti-redeposition agent <sup>3</sup>	0.5	1.0	0.8
Sodium carboxymethylcellulose	—	—	1.0
Water + perfume	65.5	56.0	59.0

<sup>1</sup> Sodium salt of a sulphated condensation product of lauryl alcohol with 2 moles of ethylene oxide.

<sup>2</sup> Phosphate ester of tridecyl alcohol condensed with seven moles of ethylene oxide.

<sup>3</sup> Example 12: VP/VA copolymer 50 : 50 ex BASF

Example 13: VP/VA copolymer 20 : 80 ex BASF

Example 14: VP/VA copolymer 60 : 40 ex BASF

## WHAT WE CLAIM IS:—

1. A detergent composition comprising a detergent active compound and a copolymer of vinylpyrrolidone and vinylacetate having an average molecular weight in the range of 10,000 to 400,000.

2. A detergent composition as claimed in claim 1, wherein said copolymer has an average molecular weight of between 20,000 and 200,000.

3. A detergent composition as claimed in claim 1 or 2, wherein the molecular ratio of vinylpyrrolidone to vinylacetate in the copoly-

mer is between 10:90 and 90:10, preferably between 30:70 and 70:30.

4. A detergent composition as claimed in claim 1, wherein the copolymer has a vinylpyrrolidone/vinylacetate ratio of 50:50.

5. A detergent composition as claimed in any of claims 1—4, wherein the copolymer is present in an amount of 0.1% to 5.0% by weight of the detergent composition.

6. A detergent composition as claimed in claim 5, wherein the copolymer is present in an amount of 0.2 to 2.0% by weight of the detergent composition.

7. A detergent composition as claimed in any of claims 1—6, which contains also sodium or potassium carboxymethylcellulose in an amount of 0.1—5.0% by weight of the composition.
8. A detergent composition according to claim 1 substantially as described in any of Examples 1—14.
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